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SUPERTRANSFERRED HYPERFINE INTERACTION IN MAGNETIC INSULATORS (II)

Perovskite-like structures

A.S. MOSKVIN
Ural State University, Sverdlovsk

N.S. OVANESYAN and V.A. TRUKHTANOV
Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

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The important mechanisms of supertransferred hyperfine (STHF) interactions in N-O-M chains are briefly discussed: (i) spin polarization of *ns* states in the N-ion due to the s-d exchange interaction, $H^{\mathrm{sd}}_{\mathrm{STHF}}$; (ii) contributions of spin-polarized states of the intervening O-ion, $H^{\mathrm{II}}_{\mathrm{STHF}}$; (iii) transfer of d-electrons of the M-ion to empty *ns* states in the N-ion, $H^{\mathrm{III}}_{\mathrm{STHF}}$. The dependence of H_{STHF} upon the N-O-M bond configuration, electronic structure, and orbital state of the M-ion is presented in a convenient form. The STHF interactions in the chains Sn^{4+}-O^{2-}-Fe^{3+}, Cr^{3+} in compounds with slightly distorted Perovskite structure are considered. The STHF field in the chain Sn^{4+}-O^{2-}-Cr^{3+} is shown to change the sign within the range of angles near 170°. This conclusion is in line with published data on the isoelectronic chain Sn^{4+}-O^2-Mn^{4+} in the compounds $Ca_{1-x}Sr_xMnO_3$. The results obtained for the N-O-Fe^{3+} chain are rationalized by the predicted angular dependence of $H_{\mathrm{STHF}} = \alpha + \beta \cos\theta + \gamma \cos^2\theta$. Features of the STHF interactions in N-O-M chains with an M-ion in an orbital degenerate state are examplified by a preliminary analysis of N-O^{2-}-V^{3+} chains in orthovanadites.

1. Introduction

In our accompanying paper [1] the supertransferred hyperfine (STHF) interaction in N-O-M chains, where N stands for non-magnetic ion, O for the intervening ion with fully occupied shells (ligand), and M for the magnetic ion with an unfilled d-shell and octahedral symmetry of the nearest neighbours, is considered on theoretical grounds. The main attention was paid to two main contributors: (i) the spin-polarization of s-electrons of the N-ion due to the s-d superexchange interaction, $H^{\mathrm{sd}}_{\mathrm{STHF}}$, and (ii) the spin-polarized states of the intervening ligand O, $H^{\mathrm{II}}_{\mathrm{STHF}}$. In particular, the expression for the operator $\hat{H}^{\mathrm{sd}}_{\mathrm{STHF}}$ is represented as

$$\hat{H}^{\mathrm{sd}}_{\mathrm{STHF}} = -\frac{8\pi}{3} g\mu_{\mathrm{B}} \sum_{n} \sum_{n'} \frac{2\hat{I}_{\mathrm{sd}}(nn')}{E(ns^2) - E(nsn's\,{}^3A_1)} \psi^*_{ns}(0)\, \psi_{n's}(0)\, (\boldsymbol{\mu}_{\mathrm{N}}\boldsymbol{S}) , \qquad (1)$$

where notation is the same as in the accompanying paper [1], and $I_{sd}(nn')$ is non-diagonal with respect to the ns-d exchange integral. The latter can be conveniently represented by isolating contributions from s-, σ- and π-bonds of M-O, i.e. e_g and t_{2g} electrons respectively.

The kinetic contribution to $I_{sd}(nn')$ is given [1] by

$$I_{sd}^{(\mathrm{kin})}(nn') = -\frac{(h_{ns} + h_{n\sigma}\cos\theta)^*(h_{n's} + h_{n'\sigma}\cos\theta)}{SU_{sd}(nn')} A_{e_g} - \frac{h^*_{n\pi} h_{n'\pi} \sin^2\theta}{SU_{sd}(nn')} A_{t_{2g}}(\varphi) , \tag{2}$$

where θ is the N-O-M angle, φ stands for asimuthal angle of the O-N bind in the local coordinate system of the M-ion with z-axis parallel to $\boldsymbol{R}_{\mathrm{MO}}$. The factors $A_{e_g}, A_{t_{2g}}(\varphi)$ are introduced here to take into consideration the type of the M-ion ground state:

$$A_{e_g} = S_{e_g} + \alpha\langle \hat{V}_0^E(\Gamma)\rangle , \tag{3}$$

$$A_{t_{2g}} = \tfrac{2}{3} S_{t_{2g}} + \beta q(\varphi) , \tag{4}$$

where the first terms in (3) and (4) describe contributions from the isotropic STHF interaction which is independent of the orbital state of the M-ion; the second terms being non-zero only for the case of orbital degenerate M-ion states and they include a combination of mean values of irreducible tensor operators of the type $\hat{V}_\nu^\gamma(\Gamma)$ in the ground state with quasimomentum Γ. The parameter α is non-zero in two cases:

$$\alpha = \begin{cases} 1 , & \text{for M-ions with configuration } t_{2g}^3 e_g^1 ({}^5E) \\ -1 , & \text{for M-ions with configuration } t_{2g}^6 e_g^3 ({}^2E) . \end{cases}$$

The expressions for the non-zero β-parameters will be as follows:

$$\beta = \begin{cases} 1 , & \text{for M-ions with configuration } t_{2g}^1 ({}^2T_2),\ t_{2g}^5 e_g^2 ({}^4T_1) \\ -1 , & \text{for M-ions with configuration } t_{2g}^2 ({}^3T_1),\ t_{2g}^4 e_g^2 ({}^5T_2) . \end{cases}$$

The mean value $\langle \hat{V}_0^E(E)\rangle$ never exceeds $\pm\frac{1}{2}$ [1], and $q(\varphi)$ varies within the range

$$-\tfrac{2}{3} \leqslant q(\varphi) \leqslant \tfrac{4}{3} , \tag{5}$$

which follows from expression (6):

$$q(\varphi) = 2\left[\langle(\cos\varphi \hat{L}_x + \sin\varphi \hat{L}_y)^2 + \hat{L}_z^2\rangle - \tfrac{4}{3}\right] , \tag{6}$$

where $\hat{L}_{x,y,z}$ are the components of the effective orbital momentum for T_1 or T_2 states.

For ions with half-filled e_g and t_{2g} shells, the corresponding A_{e_g} and $A_{t_{2g}}(\varphi)$ parameters are equal to unity. In other cases these parameters are varied within the region

$$0 \leqslant A_{e_g}(A_{t_{2g}}(\varphi)) \leqslant 2 , \tag{7}$$

and their particular values are determined by the character of the non-cubic distortions in the neighbourhood of the M-ion which are responsible for the removal of orbital degeneracy, and by the configuration of the N-O-M bond (φ-angle).

The contribution from spin-polarized states of the O-ligand to H_{STHF} may be written [1] as

$$\hat{H}^{\mathrm{II}}_{\mathrm{STHF}} = -\frac{8\pi}{3S}\mu_{\mathrm{B}}\Big[N_s^4\,\Big|\lambda_s\sum_n \mathcal{D}(f_0 n_0 s - f_N ns)\,\varphi_{ns}(0)\Big|^2$$

$$+ N_\sigma^4\,\Big|\lambda_\sigma\sum_n \mathcal{D}(f_0 n_0 p - f_N ns)\,\varphi_{ns}(0)\Big|^2 \cos^2\theta\, A_{e_g}$$

$$+ N_\pi^4\,\Big|\lambda_\pi\sum_n \mathcal{D}(f_0 n_0 p - f_N ns)\,\varphi_{ns}(0)\Big|^2 \sin^2\theta\, A_{t_{2g}}(\varphi)\Big](\boldsymbol{\mu}_N \boldsymbol{S})\,, \tag{8}$$

where $D(f_0 n_0 l_0 - f_N ns)$ are either parameters of transfer or of O-N overlapping; $N_{\mathrm{s},\sigma,\pi}$ are normalizing factors for s-, σ- and π-orbitals of the ligand, and $\lambda_{\mathrm{s},\sigma,\pi}$ are covalency parameters.

For the sake of completeness let us write the expression for the contribution of admixing of ns states in the N-ion with the d-state in the M-ion to H_{STHF}. This mechanism was first taken into account by Huang et al. [2]; the generalization up to an arbitrary M-ion with the $t_{2\mathrm{g}}^{n_1} e_{\mathrm{g}}^{n_2}$ configuration results in

$$\hat{H}^{\mathrm{III}}_{\mathrm{STHF}} = -\frac{8\pi}{3S}\mu_{\mathrm{B}}\Big[\Big|\sum_n (b_{ns} + b_{n\sigma}\cos\theta)\,\varphi_{ns}(0)\Big|^2 A_{e_g}$$

$$+ \Big|\sum_n b_{n\pi}\varphi_{ns}(0)\Big|^2 \sin^2\theta\, A_{t_{2g}}(\varphi)\Big](\boldsymbol{\mu}_N \boldsymbol{S})\,, \tag{9}$$

where $b_{ns,n\sigma,n\pi}$ are determined either as N-M overlapping parameters for occupied ns states,

$$b_{ns} = \lambda_s S(f_0 n_0 s - f_N ns)\,, \qquad b_{n\sigma,\pi} = \lambda_{\sigma,\pi} S(f_0 n_0 p - f_N ns)\,, \tag{10}$$

or as transfer parameters of the d-electron into the empty ns state,

$$b_{ns,\sigma,\pi} \approx h_{\mathrm{s},\sigma,\pi}(\mathrm{d} - ns)/U_{\mathrm{d}ns}\,, \tag{11}$$

where $h_{\mathrm{s},\sigma,\pi}(\mathrm{d}\text{-}ns)$ stands for the d-ns transfer integral due to the definite s-, σ and π M-O bond, and $U_{\mathrm{d}ns}$ is the mean value of the transfer energy.

The expressions given above for $H^{\mathrm{II,III}}_{\mathrm{STHF}}$ were derived under the assumption that effects of intra-atomic exchange for the electron transfer processes in the M-ion are negligible in the M-O-N system. These effects seem to be of particular importance for ions of $t_{2\mathrm{g}}^{1,2,3}$ configurations with an empty e_{g} subshell. Moskvin et al. [1] have demonstrated that intra-atomic exchange may be taken into consideration by the use of modified spectroscopic coefficients $V^{(a\gamma)}$ for $H^{\mathrm{sd}}_{\mathrm{STHF}}$, or by the use of covalency parameters $\lambda^{\uparrow,\downarrow}_{\mathrm{s},\sigma,\pi}$ [1,3] for $H^{\mathrm{II}}_{\mathrm{STHF}}$.

The positive value of the hyperfine magnetic field which is induced on the N-nucleus at positively directed spin in the M-ion seems to be of particular interest in the STHF interactions determined by the $H^{\mathrm{II,III}}_{\mathrm{STHF}}$ contributions (8, 9). This is valid for any M-ion with an unfilled d-shell, especially if the positive values of A_{e_g}, $A_{t_{2g}}(\varphi)$ are kept in mind.

Additional contributions for instance to $H^{\mathrm{II}}_{\mathrm{STHF}}$, due to intra-atomic exchange in the M-ion, would result in negative values for the hyperfine field at the M-nucleus, independently of the type of M-ion.

The following circumstances should be kept in mind when the value and the "sign" of exchange polarization mechanism (1) are determined:

(i) There are two contributions to the $I_{\mathrm{sd}}(nn')$ value – kinetic and potential exchange and they are of opposite sign.

(ii) The kinetic contribution to $I_{\mathrm{sd}}(nn')$ is substantially dependent on the transfer energy $U_{\mathrm{sd}}(nn')$, the evaluation of which contain considerable difficulties.

(iii) The sign of the $\varphi_{n\mathrm{s}}(0)$ values is dependent on n, for instance, in the case of Sn [4],

$$\varphi_{3\mathrm{s}}(0) = 43.96 \text{ a.u.}, \qquad \varphi_{4\mathrm{s}}(0) = -19.87 \text{ a.u.}, \qquad \varphi_{5\mathrm{s}}(0) = 7.12 \text{ a.u.}$$

(iv) The quantity n, rigorously speaking, is not a "good" quantum number. The molecular orbital $\psi_{na_{1g}}$ is represented by the linear combination of atomic wave functions φ_{ns} with different n-values.

(v) The necessity of accounting for contributions from the number of ns and n's states may be demonstrated by the example of $H^{\mathrm{sd}}_{\mathrm{STHF}}$. The analysis of overlapping integrals of the type $S(f_0 n_0 l_0 - f_N ns)$ implies that the O-N interaction is strongly increased upon an increase in n. In the case of Sn-O ($R_{\mathrm{Sn\text{-}O}} = 2$ Å)

$$|S(5\mathrm{s}\text{-}2\mathrm{p})| = 0.2337\,, \qquad |S(4\mathrm{s}\text{-}2\mathrm{p})| = 0.0379\,, \qquad |S(3\mathrm{s}\text{-}2\mathrm{p})| = 0.0062\,. \tag{12}$$

The increase in the $I_{\mathrm{sd}}(nn')$ parameters with an increase in n' is enhanced and also by a decrease of $U_{\mathrm{sd}}(nn')$ values. It should be noted that the value of $U_{\mathrm{d}ns}$ for the process of d-electron transfer into the empty n's state in the N-ion is increased together with n'. The fall off in $\varphi_{n'\mathrm{s}}(0)$ and $\{E(ns^2) - E(nsn's^3A_1)\}$ values with an increase in n' is less pronounced relative to the increase in overlapping and probably in the transfer parameters of the type $\mathcal{D}(f_0 n_0 l_0 - f_{\mathrm{N}} ns)$, so that a series in n and n' for $H^{\mathrm{sd}}_{\mathrm{STHF}}$ seems to be slowly convergent and probably sign alternating.

It would appear that the "sign" of the exchange-polarization STHF mechanism could be obtained from the following simple considerations. For one ns electron, kinetic s-d exchange results in antiferromagnetic spin coupling between ns and d electrons, while potential exchange would result in ferromagnetic coupling. This is due to a rigid determination of the $I_{\mathrm{sd}}(nn)$ parameters which are diagonal in n. Antiferromagnetic coupling corresponds to the situation when ns electrons with "down" spin are drawned to an M-ion which promotes induction of the positive STHF field on N-nucleus. For the case of ferromagnetic s-d coupling the situation is opposite.

However, the spin-polarization effects for ns^2 states is in fact determined by non-diagonal parameters $I_{sd}(nn')$, $n \neq n'$, and as is seen from considerations given above, the problem of the determination of the H^{sd}_{STHF} "sign" appears to be rather complicated.

Nevertheless in our opinion the assumption of "normal signed" H^{sd}_{STHF}, when the kinetic contribution to $I_{sd}(nn')$ leads to a positive STHF field and the potential contribution to a negative field, seems to be rather reasonable. It will be shown further that this is consistent with the experimental data, at least for the Sn^{4+}-O^{2-}-M system.

2. Perovskite-like structures

A wide class of magnetic dielectrics with orthorhombic slightly distorted Perovskite structure (symmetry group D^{16}_{2h}) is known. Compounds of the type RMO_3, where M is Fe, Cr or V, and R is a rare earth or yttrium atom, are known to display a number of most interesting magnetic properties and to promise fruitful practical applications.

Investigations of the N-O-M STHF interaction in doped compounds $RM_{1-x}N_xO_3$, where N is a non-magnetic ion, e.g. Sn^{4+}, are interesting in several respects. First of all only one type of STHF interaction can be taken into account in the N-O-M chain at a bond angle θ within the range 140–156°. Second, the configuration of the N-O-M chain is regularly dependent on the type of rare-earth ion, and this enables us to investigate the angular dependence of H_{STHF}. Contributions of rare-earth ions up to temperatures of $\approx 10^\circ$K are, in fact, limited to the change of the N-O-M angle. Third, consideration of M-ions of the type Fe^{3+}, Cr^{3+}, V^{3+} provides an opportunity to investigate the influence of such factors as M-ion ground state structure, and the relative role of s-, σ- and π-bonds, etc., on H_{STHF}. The H_{STHF} value and the character of its changes are sensitive to magnetic structure, and they can be applied to the determination of the latter.

The M-ions occupy four magnetic non-equivalent positions [5] in the elementary RMO_3 cell:

$$M_1(0, \tfrac{1}{2}, 0)\,, \qquad M_2(0, \tfrac{1}{2}, \tfrac{1}{2})\,, \qquad M_3(\tfrac{1}{2}, 0, \tfrac{1}{2})\,, \qquad M_4(\tfrac{1}{2}, 0, 0)\,.$$

The structure of the closest neighbourhood of $M_4(\frac{1}{2}, 0, 0)$ is shown in fig. 1. The local crystalline field axes of M-ions are rearranged by rotation about 180° around the a, b, c axes. The configuration of the non-magnetic neighbourhood around the M-ion formed by six O^{2-} ions may be represented by a slightly distorted octahedron, the distortions being similar in magnitude for all M_i ions in local crystalline field axes.

Let ion M_4 (fig. 1) be replaced by the non-magnetic N-ion. For the sake of convenience let us introduce a new local coordinate system for every surrounding M-ion in which the z-axis is directed to the oxygen ion forming the N-O-M bond. The "old"

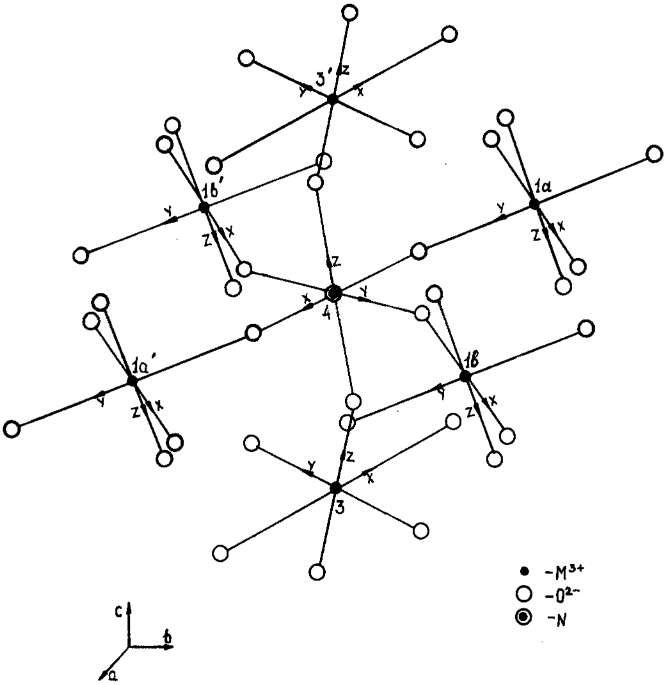

Fig. 1. Geometry of the N-O^{2-}-M^{3+}-O^{2-} bonds in RMO_3 compounds.

local axes will be therefore transformed according to

$$M_3:\ x,y,z\to x,y,z\ ;\qquad M_{3'}:\ x,y,z\to y,x,-z\ ;$$
$$M_{1a}:\ x,y,z\to x,-z,y\ ;\qquad M_{1a'}:\ x,y,z\to y,z,x\ ;$$
$$M_{1b}:\ x,y,z\to z,x,y\ ;\qquad M_{1b'}:\ x,y,z\to -z,y,x\ .$$

The mean values of the irreducible tensor operators $\hat{V}^{\gamma}_{\nu}(\Gamma)$ [1], or combinations fo the orbital momentum operators in the "new" local systems will be related to those in the "old" systems or the M_3 coordinate system by

$$\begin{aligned}
&M_3:\ \langle V_0^E\rangle = A\ ,\qquad \langle V_2^E\rangle = B\ ,\qquad \langle V_2^{T_2}\rangle = C\ ;\\
&M_{3'}:\ \langle V_0^E\rangle = A\ ,\qquad \langle V_2^E\rangle = -B\ ,\qquad \langle V_2^{T_2}\rangle = C\ ;\\
&M_{1a}:\ \langle V_0^E\rangle = -\tfrac{1}{2}A - \tfrac{1}{2}\sqrt{3B}\ ,\qquad \langle V_2^E\rangle = -\tfrac{1}{2}\sqrt{3}A + \tfrac{1}{2}B\ ;\\
&M_{1a'}:\ \langle V_0^E\rangle = -\tfrac{1}{2}A - \tfrac{1}{2}\sqrt{3}B\ ,\qquad \langle V_2^E\rangle = \tfrac{1}{2}\sqrt{3}A - \tfrac{1}{2}B\ ;\\
&M_{1b}:\ \langle V_0^E\rangle = -\tfrac{1}{2}A + \tfrac{1}{2}\sqrt{3}B\ ,\qquad \langle V_2^E\rangle = -\tfrac{1}{2}\sqrt{3}A - \tfrac{1}{2}B\ ;\\
&M_{1b'}:\ \langle V_0^E\rangle = -\tfrac{1}{2}A + \tfrac{1}{2}\sqrt{3}B\ ,\qquad \langle V_2^E\rangle = \tfrac{1}{2}\sqrt{3}A + \tfrac{1}{2}B\ .
\end{aligned}\tag{13}$$

The M_3 and $M_{3'}$, M_{1a} and $M_{1a'}$, M_{1b} and $M_{1b'}$ ions contribute to H_{STHF} equally since crystallographically they are related by the operation of inversion about the N-ion. The contributions of such pairs are generally different in magnitude, though a rigorous relation between them can be established in the case of axial distortions when the only non-zero mean value among A, B, C ... is A: orbital isotropic contributions from all M_i ions are actually the same, orbital anisotropic contributions from M_i ions are the same in the *ab* plane and equal to half of the orbital anisotropic contribution from M_3 (or $M_{3'}$) with the reverse sign.

3. Orbital non-degenerate M-ions

Let us consider in detail the simplest case of Fe^{3+} or Cr^{3+} with ground orbital non-degenerate states of $^6A_1$ or $^4A_2$ as M-ions. The hyperfine field at the N-nucleus is determined by similar (with the accuracy of $\theta_1 \simeq \theta_2$ [5,6]) orbital isotropic contributions from six M_i ions. It is assumed, of course, that the configuration in the magnetic neighbourhood of the N-ion is not changed with a pure compound, i.e. of *G*-type [7].

Since the π-bond is dominant, a remarkably weak STHF interaction is expected in the N-O^{2-}-Cr^{3+} chain. For the speculative case of $\theta = 180°$ the small negative contributions from *s*- and σ-bonds ($|\lambda^{\downarrow}_{s,\sigma}|^2 < |\lambda^{\uparrow}_{s,\sigma}|^2, S_z = S$) should be included in H_{STHF} [1]. The exchange polarization term $H^{\mathrm{sd}}_{\mathrm{STHF}}$ is expected to be "normal" in sign. It includes small contributions from the potential s-d(t_{2g}) exchange and also kinetic exchange due to *ns* electron transfer to the empty e_g states in the Cr^{3+} ion. If in the N-O^{2-}-Cr^{3+}chain $\theta = 90°$, the value of H_{STHF} is positive and its value is the result of contributions from the π-bond to $H^{\mathrm{II,III}}_{\mathrm{STHF}}$ and $H^{\mathrm{sd}}_{\mathrm{STHF}}$, the main role being played by antiferromagnetic kinetic s-d(t_{2g}) exchange in the latter case. Therefore, at some angle probably close to 180° the value of H_{STHF} in the N-O^{2-}-Cr^{3+} chain might have its sign reversed.

This line of reasoning is supported by the results of experimental investigations of the STHF field in $\mathrm{RCrO_3}$ doped with Sn^{4+} [8] (fig. 2). The angular dependence of H_{STHF} may be approximated

$$H_{\mathrm{STHF}} = H_{90°} \sin^2\theta + H_{180°} \cos^2\theta \,, \tag{14}$$

at $H_{90°} = 239$ kOe, $H_{180°} = -8$ kOe. The small contribution proportional to $\cos\theta$ is negligible in (14): its value seems to be positive at $\theta \to 180°$, but it will not be able to compensate for important negative items.

Hence within the range of angles $\theta \approx 170°$ a reverse in sign of the hyperfine field should be observed. This conclusion is theoretically valid for the Sn^{4+}-O^{2-}-Mn^{4+} chain as well, where the Mn^{4+} ion is isoelectronic to the $\mathrm{Cr}^{3+}(t^3_{2g}, {}^4A_2)$ ion.

To our mind, the results of Takano et al. [9] may be regarded as experimental support for this prediction. The STHF field induced at $^{119}\mathrm{Sn}$ nuclei in $\mathrm{Ca}_{1-x}\mathrm{Sr}_x\mathrm{MnO_3}$ compounds was shown to reverse its sign at $x \approx 0.875$. These compounds are

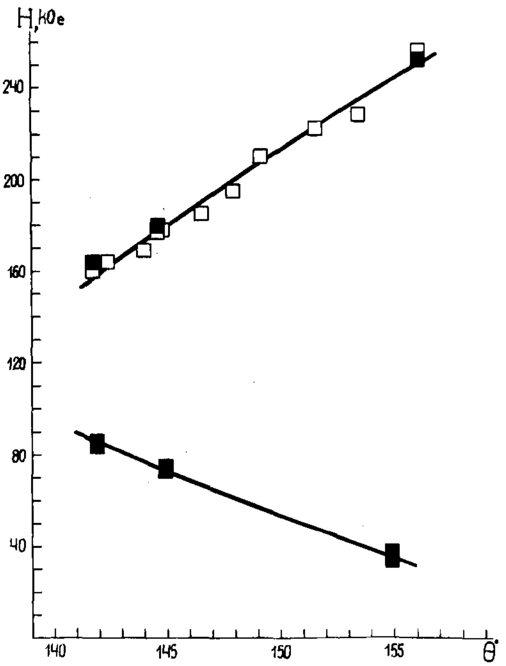

Fig. 2. Hyperfine field at the ^{119}Sn nucleus as a function of the average bond angle $\bar{\theta}$ in orthoferrites (upper curve) and orthochromites (lower curve). Experimental data and $\bar{\theta}$ are given with their experimental uncertainties; solid squares from paper [8], open squares from paper [15].

known [10,11] to have Perovskite-like structure, and orthorhombic distortions are decreased upon an increase in the Sr concentration, so that the pure $SrMnO_3$ has an ideal cubic Perovskite structure [10]. The independence of the isomer shift in the ^{119}Sn Mössbauer spectra of the composition implies that the Sn^{4+}-O^{2-} distance is constant and independent of the concentration x. This is evidently valid for the Mn^{4+}-O^{2-} distance judging from the findings [11] that in the number of $Ca_{1-x}Sr_x$-MnO_3 compounds it is constant and equal to ≈1.90 Å. A similar behaviour is also inherent in the number of ABO_3 compounds with Perovskite structures: $RAlO_3$, $RFeO_3$, $RCrO_3$, where the influence of the R-ion is limited to changes in the B-O-B bond geometry. At a fixed Mn-O distance in $Ca_{1-x}Sr_xMnO_3$, the mean value of the Mn^{4+}-O^{2-}-Mn^{4+} bond angle should vary from ≈157° in pure $CaMnO_3$ to 180° (linear chain) in $SrMnO_3$. According to the predictions of the theory of angular dependence of superexchange [12,13] this would result in a rise of the Neel temperature with an increase in the Sr^{2+} concentration, and on the other hand, in a fall off in the Dzjaloshinsky interaction [13], or the weak ferromagnetic momentum, down to zero in $SrMnO_3$. This is in agreement with the experimental data available [10,11].

Angular dependence parameters of the type (14) for H_{STHF} on ^{119}Sn nuclei in

$Ca_{1-x}Sr_xMnO_3$ can be evaluated on the basis of the Takano et al. data [9]:

$$H_{90^\circ} \simeq 609 \text{ kOe}\,, \qquad H_{180^\circ} \approx -20 \text{ kOe}\,, \tag{15}$$

where somewhat higher values of these parameters compared to that of ^{119}Sn in $RCrO_3$ may be rationalized if it is assumed that in the simplest approximation

$$\frac{H_{90^\circ}(Cr^{3+})}{H_{90^\circ}(Mn^{4+})} \approx \frac{f_\pi(Cr^{3+})}{f_\pi(Mn^{4+})}\,, \qquad \frac{H_{180^\circ}(Cr^{3+})}{H_{180^\circ}(Mn^{4+})} \approx \frac{f_\sigma(Cr^{3+})}{f_\sigma(Mn^{4+})}\,,$$

and that the covalency parameters f_π, f_σ for the Mn^{4+}-O^{2-} bond in $CaMnO_3$ are almost twice as high in magnitude than that for the Cr^{3+}-O^{2-} bond in orthochromites [14].

The main role in N-O^{2-}-Fe^{3+} chains is played by the strong σ-bond. The $H^{\mathrm{II}}_{\mathrm{STHF}}$ is positive at any θ and is increased with the rise of θ $(|\lambda^{\downarrow}_{\sigma}|^2 > |\lambda^{\downarrow}_{\pi}|^2)$. The contributions of $H^{\mathrm{sd}}_{\mathrm{STHF}}(\mathrm{kin})$ and $H^{\mathrm{III}}_{\mathrm{STHF}}$ behave in a similar manner, although the predicted angular dependence may appear to be different due to terms proportional to $\cos\theta$. The negative contribution from the potential s-d exchange is negligible compared to the kinetic contribution at $\theta \approx 180^\circ$, but competitive at $\theta \approx 90^\circ$, since the positive kinetic contribution is determined in this case by the weak π-bond for the Fe^{3+} ion (see table 1).

The H_{STHF} values for Sn^{119} nuclei in $RFeO_3$ were experimentally defined in [8,15]. Their dependencies on the bond angle θ are depicted in fig. 2. As expected, these data are not fully rationalized when only $H^{\mathrm{II}}_{\mathrm{STHF}}$ is taken into consideration. According to eq. (8) $H_{90^\circ} < 0$, which is not consistent with the conclusion that $H^{\mathrm{II}}_{\mathrm{STHF}} > 0$ within the full range of θ. The observed $H_{\mathrm{STHF}}(\theta)$ dependence is in line with the existence of a strong negative contribution of potential s-d exchange at $\theta \to 90^\circ$.

Under the assumption that the angular dependence of the total hyperfine field on the Sn^{119} nucleus in $RFeO_3$ (fig. 2) has the form

$$H_{\mathrm{STHF}} = \alpha + \beta\cos\theta + \gamma\cos^2\theta\,, \tag{16}$$

Table 1
The f_s, f_σ and f_π values (%) for Fe^{3+}-O^{2-} and Cr^{3+}-O^{2-} bonds

	Fe^{3+}-O^{2-}			Cr^{3+}-O^{2-}		
	a)	b)	c)	a)	b)	c)
f_s	0.8 ± 0.2	1.05	1.0		−0.14 ± 0.03	0
f_σ	5.5 ± 0.7	6.8 ± 0.6	5.0	−2.2 ± 0.6	−3.6 ± 0.9	−0.7
f_π	2.1 ± 0.3	1.1 ± 0.4	2.0	2.7 ± 0.6	3.5 ± 0.6	4.0

a) Ref. [14].
b) Ref. [22].
c) Ref. [23].

we have defined parameters α, β, γ: $\alpha = 8$ kOe, $\beta = 241$ kOe and $\gamma = 551$ kOe. A large value for the β-parameter implies the important role of the s-electrons in the O^{2-} ion in the STHF interaction in Sn^{4+}-O^{2-}-Fe^{3+}.

In Fe^{3+}-$6O^{2-}$ complexes the s-bond competes with the π-bond in magnitude (table 1). If to admit that the overlapping and transfer parameters 2p → n's, 2s → n's of the O^{2-}-Sn^{4+} bond are in the same correlation as the corresponding O^{2-}-Fe^{3+} bond parameters, it would be then reasonable to suppose the following correlation between $b_{ns}, b_{n\sigma}$ in (9) and $h_{ns}, h_{n\sigma}$ in (2) takes place:

$$\frac{b_{ns}}{b_{n\sigma}} \approx \frac{h_{ns}}{h_{n\sigma}} \approx \frac{\lambda_s^2}{\lambda_\sigma^2} = \frac{f_s}{f_\sigma} \approx 0.15\text{–}0.20\,,$$

according to the data of table 1. Therefore, the β-value in (16) may reach 30–40% from the Fe^{3+}-O^{2-} σ-bond contribution into γ, which is supported by a best fitting procedure. As follows from the simplest considerations about orbital signs (fig. 3, $\theta = 180^\circ$), the sign of β should be positive; this is also in accordance with the present calculation.

The magnitude of the α-parameters provides information on the rectangular STHF interaction Sn^{4+}-O^{2-}-Fe^{3+}. At $\theta = 90^\circ$, the σ-bond Fe^{3+}-O^{2-} in $H^{\mathrm{II,III}}_{\mathrm{STHF}}$, $H^{\mathrm{sd}}_{\mathrm{STHF}}(\mathrm{kin})$ does not contribute to the STHF field. Contribution of the π-bond Fe^{3+}-O^{2-} to H_{STHF} may be expressed by means of the analogous contribution in the Sn^{4+}-O^{2-}-Cr^{3+} chain

$$\alpha_\pi \approx \frac{f_\pi(\text{Fe-O})}{f_\pi(\text{Cr-O})} H_{90^\circ}(Cr^{3+}) \approx 75\text{–}200\ \text{kOe}\,,$$

in accordance with (14) and the data of table 1. The small contribution of the s-bond Fe^{3+}-O^{2-} to the STHF field is positive for $H^{\mathrm{II,III}}_{\mathrm{STHF}}$ mechanisms and probably also for $H^{\mathrm{sd}}_{\mathrm{STHF}}(\mathrm{kin})$. Hence, the low value of $\alpha \approx 8$ kOe can hardly be explained without a relatively large negative contribution of the s-d(e_g) potential exchange to $H^{\mathrm{sd}}_{\mathrm{STHF}}$ being taken into account.

In the theoretical analysis of experimental data on H_{STHF} for ^{119}Sn nuclei, orthochromites and orthoferrites of rare earths and yttrium we assumed the bond angle θ in the Sn^{4+}-O^{2-}-M^{3+} chain to be equal to that of Fe^{3+}-O^{2-}-Fe^{3+} or Cr^{3+}-O^{2-}-Cr^{3+} in corresponding pure compounds. The validity of this approximation may follow from the equal ionic radii of Fe^{3+} (0.67 Å), Cr^{3+} (0.64 Å) and Sn^{4+} (0.67 Å). Charge compensation is reached by Ca^{2+} ions introduced in the rare-earth sublattice. It is worthwhile noting that the ionic radius of Ca^{2+} (1.04 Å) is equal to that of La^{3+} (1.04 Å).

Expression (16) may be applied to rationalize the angular dependence of the STHF interaction ^{57}Fe-O^{2-}-Fe^{3+} in orthoferrites. Experimental data [16] [†] together

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[†] Low temperature NMR data [16] seem be more reliable compared with that of Mössbauer spectroscopy [17]; the latter were discussed previously [3] from the point of view of the angular dependence of $H^{\mathrm{II}}_{\mathrm{STHF}}$. The NMR data were shown [16] to be hardly rationalized if only $H^{\mathrm{II}}_{\mathrm{STHF}}$ were taken into account.

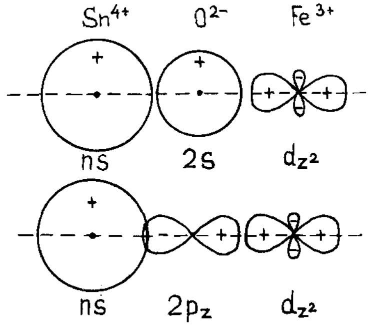

Fig. 3. Orbitals involved in s- and σ-bonding.

with the theoretical predictions for $RFeO_3$ are given in fig. 4. The agreement is much better compared with the case [16] when only the H^{II}_{STHF} contribution was taken into account.

It should also be noted that the interpretation of experiments given above is reasonable when the effects of slight deviations in Sn^{4+}-O^{2-}, Fe^{3+}-O^{2-} and Cr^{3+}-O^{2-} distances are neglected. To estimate the magnitude of these effects, a quantity $dH_{STHF}/d\epsilon$, where ϵ is the isotropic deformation, is needed. Representing $dH_{STHF}/d\epsilon = (dH_{STHF}/dp)E$, where p is the pressure and E is the Young modulus for H_{STHF}

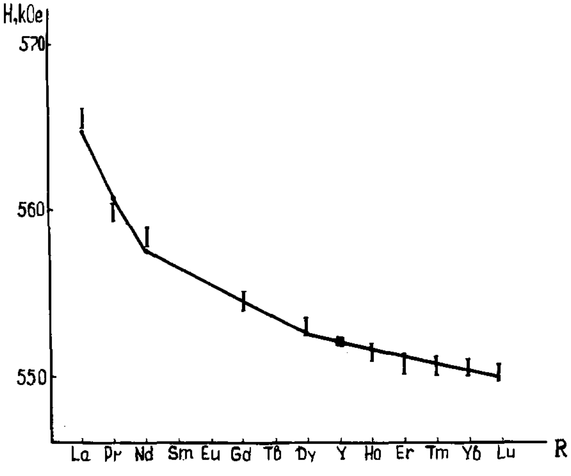

Fig. 4. Experimental data of the NMR measurements of a hyperfine field on ^{57}Fe in $RFeO_3$ given with their experimental errors and fitted values (solid curve). In the case of $YFeO_3$ we took the value 552 kOe from the Mössbauer data ($T = 4.2°K$) by C.W. Durbin et al. [24].

on ^{57}Fe in orthoferrites [18] †

$$\mathrm{d}H_{\mathrm{STHF}}/\mathrm{d}p \approx 0.1 \text{ kOe/kbar}$$

and $E = 2 \times 10^{12}$ erg/cm^3 [19], we get $\mathrm{d}H_{\mathrm{STHF}}/\mathrm{d}\epsilon \approx -2 \times 10^2$ kOe. The maximal possible deviation of the Fe^{3+}-O^{2-} separation from the mean value 2.011 Å is near 0.3% in $\mathrm{LaFeO_3}$ [5]. Hence the account of these effects would result in errors of the order of 0.5 kOe, i.e. of the same order as the experimental accuracy. Similar conclucions may be drawn for other cases discussed in this paper.

It seems to be difficult to give reliable quantitative predictions, even for the simplest cases, for the contributions of $H_{\mathrm{STHF}}^{\mathrm{II}}$ to hyperfine fields at nuclei of non-magnetic ions. Some covalency parameters necessary in such calculations are given in table 1. These parameters vary by not more than a factor of two, if Fe^{3+} ions in orthoferrites or isostructural orthoaluminates are considered. But this is not the case for the f_s and f_σ parameters for the Cr^{3+} ion. Ambiguities in these data together with complicated calculations of the $\mathcal{D}(n_0 l_0 - Nns)$ parameters of the Sn^{4+}-O^{2-} bond leave room for a qualitative analysis only for the $H_{\mathrm{STHF}}^{\mathrm{II}}$ contribution. However, attempts based only on $H_{\mathrm{STHF}}^{\mathrm{II}}$ were reported in the literature [3]. As a rule, this leads to an overestimate of the f_σ and f_π parameters.

As for the problem of numerical calculations of the H_{STHF} magnitude, the high sensitivity of the results to the choice of the basic method of calculation (group orbitals, independent bond, etc.) should be emphasized. In the case of N-6O^{2-}-6M^{3+} complexes (fig. 1) in the $\mathrm{RMO_3}$ compound the group orbitals method appears to be extremely difficult due to the low symmetry of the surrounding N-ion, even for the purposes of qualitative analysis. This method is apparently much more convenient if applied to highly symmetrical N-6O^{2-}-6M^{3+} complexes. The method of independent bonds in the latter case may give incorrect H_{STHF} values.

4. Orbital degenerate M-ions

The orthovanadites $\mathrm{RVO_3}$ activated by non-magnetic Sn^{4+}-type ions are of considerable interest in studies of STHF interactions. The V^{3+} ion in its $t_{2g}^2(^3T_1)$ ground state displays a threefold orbital degeneracy which is removed by non-cubic distortions, whereas distortions in orthoferrites and orthochromites practically have no influence on the hyperfine field value. In doped $\mathrm{RVO_3}$ the value, and probably the sign, of H_{STHF} are strongly dependent upon these distortions. Let us define that upon stretching along the x, y, z axes, which are coincident with the fourth order axes, the corresponding states $|^3T_1x\rangle$, $|^3T_1y\rangle$, $|^3T_1z\rangle$ are stabilised and we examine the $H_{\mathrm{STHF}}^{\mathrm{II}}$ changes caused by these distortions. Only the contribution from the π-

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† It should be noted that the value of $d(H_{\mathrm{cov}} + H_{\mathrm{STHF}})/dp$ was evaluated [18], where H_{cov} is the so-called covalent contribution [3], but that it is the H_{STHF} term which gives the dominant contribution to this derivative.

bond is to be considered for the sake of brevity. The orbital isotropic contribution to $H^{\mathrm{II}}_{\mathrm{STHF}}$ is given by

$$H^{\mathrm{II}}_{\mathrm{STHF}}(\mathrm{isotr}) = \frac{8\pi}{3}\mu_{\mathrm{B}}N^4\,\{|\lambda^{\downarrow}_{\pi}|^2 - \tfrac{1}{3}|\lambda^{\uparrow}_{\pi}|^2\}\,d_p\,\sin^2\theta\,, \tag{17}$$

the meaning of the d_p parameters being given in the accompanying paper [1]. Now let us calculate the orbital anisotropic contribution for the following important cases:

(i) The deformation is along the x-axis. The mean non-zero values of $\langle\hat{V}^{\gamma}_{\nu}(\Gamma)\rangle$ are

$$\langle\hat{V}^{A_1}_{0}(T_1)\rangle = \sqrt{\tfrac{1}{3}}\,, \qquad \langle\hat{V}^{E}_{0}(T_1)\rangle = -\sqrt{\tfrac{1}{3}}\,.$$

Using the data of table 1 in [1] we get

$$H^{\mathrm{II}}_{\mathrm{STHF}}(\mathrm{anis}) = \frac{8\pi}{3}\mu_{\mathrm{B}}N^4\,\tfrac{1}{3}|\lambda^{\uparrow}_{\pi}|^2\,d_p\,\sin^2\theta\,. \tag{18}$$

(ii) The deformation is along the x-axis. The non-zero averaged values are

$$\langle\hat{V}^{A_1}_{0}(T_1)\rangle = \sqrt{\tfrac{1}{3}}\,, \qquad \langle\hat{V}^{E}_{0}(T_1)\rangle = \tfrac{1}{2}\sqrt{\tfrac{1}{3}}\,, \qquad \langle\hat{V}^{E}_{2}(T_1)\rangle = -\tfrac{1}{2}\,,$$

and therefore

$$H^{\mathrm{II}}_{\mathrm{STHF}}(\mathrm{anis}) = \tfrac{4}{3}\pi\,\mu_{\mathrm{B}}N^4\,|\lambda^{\uparrow}_{\pi}|^2\,d_p\,\sin^2\theta(\cos 2\varphi - \tfrac{1}{3})\,. \tag{19}$$

(iii) The deformation is along the y-axis. The non-zero averages are

$$\langle\hat{V}^{A_1}_{0}(T_1)\rangle = \sqrt{\tfrac{1}{3}}\,, \qquad \langle\hat{V}^{E}_{0}(T_1)\rangle = \tfrac{1}{2}\sqrt{\tfrac{1}{3}}\,, \qquad \langle\hat{V}^{E}_{2}(T_1)\rangle = \tfrac{1}{2}\,,$$

and therefore

$$H^{\mathrm{II}}_{\mathrm{STHF}}(\mathrm{anis}) = -\tfrac{4}{3}\pi\,\mu_{\mathrm{B}}N^4\,|\lambda^{\uparrow}_{\pi}|^2\,d_p\,\sin^2\theta(\cos 2\varphi + \tfrac{1}{3})\,. \tag{20}$$

It may be shown from a comparison of (17)–(20) that non-cubic distortions of crystalline field around the M-ion, via the influence on the orbital anisotropic part of the STHF interaction, causes substantial changes in magnitude, sign and angular dependence of the hyperfine field on the N-nucleus. An orbital anisotropy and non-cubic distortions can also result in different values, and even signs, of superexchange V^{3+}-O^{2-}-V^{3+} interactions between the nearest neighbours in orthovanadites. It may be responsible for the fact [20] that RVO_3 reveals magnetic structures different from those of simple G-type in orthoferrites and orthochromites. For instance, a phase transition from a G- to C-structure in YVO_3 was found near 80°K [21].

Besides this particular interest the Mössbauer studies of these phase transition may provide useful information about the orbital anisotropy of the STHF interaction as may be shown as follows. If non-cubic distortions of V^{3+}-$6O^{2-}$ octahedrons have an axial character, then the only non-zero averages in the M_3 local coordinate system are $\langle\hat{V}^{A_1}_{0}(T_1)\rangle, \langle\hat{V}^{E}_{0}(T_1)\rangle = A$. Assuming $\theta_1 \approx \theta_2$ (RVO_3 is close to orthoferrites from a crystallographic point of view), we get

(a) for the isotropic contribution

$$H_{\mathrm{STHF}}(\mathrm{isotr}) = \begin{cases} 6h(\mathrm{isotr}), & \text{G-structure} \\ 2h\,(\mathrm{isotr}), & \text{C-structure}\,; \end{cases} \tag{21}$$

(b) for the anisotropic contribution

$$H_{\mathrm{STHF}}(\mathrm{anis}) = \begin{cases} 0 \,, & \text{G-structure} \\ -4h(\mathrm{anis}) \,, & \text{C-structure} \,, \end{cases} \tag{22}$$

where h(isotr) is the isotropic contribution from any separated N-O^{2-}-V^{3+} bond, h(anis) is the anisotropic contribution from the N-O^{2-}-V_3^{3+} bond, and the positive spin direction is that of the M_1 ion (fig. 1).

Therefore, the orbital anisotropy of the H_{STHF} may be separated on the basis of the experimental data on the STHF interaction measurements in orthovanadites with magnetic structural transition.

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